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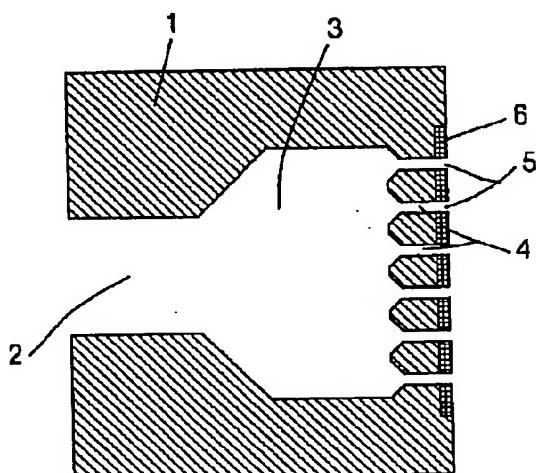
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(54) 【発明の名称】 発泡性熱可塑性樹脂粒子の製造法

(57) 【要約】

【構成】 発泡剤含有熱可塑性樹脂、例えばポリスチレンとブタンの溶融混練物を、ペレタイズ用ダイス内に導入してダイスの押出孔に向けて流路を流动させ、次いでこの流路よりも流路断面積の大きい流路、例えば2~10倍の流路断面積をもつ流路に流入させて、溶融混練物中に応力を緩和させた後、押出孔を通過させ、その出口から加圧液中に押し出し、即時切断して粒子とし、次いで冷却する。

【効果】 発泡剤含有熱可塑性樹脂の溶融混練物が溶融混練押出で受けた応力を、ペレタイズ用ダイス内で大きく緩和させることができため、残留応力の少ない良好な発泡粒子を容易に製造できる。



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## 【特許請求の範囲】

【請求項1】 発泡剤含有熱可塑性樹脂の溶融混練物を、ペレタイズ用ダイス内に導入してダイスの押出孔に向けて流路を流動させ、次いでこの流路よりも流路断面積の大きい流路に流入させた後、押出孔を通過させ、その出口から加圧液中に押出し、即時切断して粒子とし、次いで冷却することを特徴とする発泡性熱可塑性樹脂粒子の製造法。

【請求項2】 ダイス内に導入された発泡剤含有熱可塑性樹脂の溶融混練物を、複数の流路に流入させ、次いでそれぞれの流路よりも流路断面積の大きい流路に流入させた後、押出孔を通過させる請求項1記載の製造法。

【請求項3】 ダイス内に導入させた発泡剤含有熱可塑性樹脂の溶融混練物を、この流路よりも流路断面積の大きい流路に流入させた後、複数の押出孔を通過させる請求項1記載の製造法。

【請求項4】 熱可塑性樹脂が、芳香族ビニル系樹脂である請求項1、2または3記載の製造法。

【請求項5】 热可塑性樹脂が、スチレン系樹脂である請求項1、2又は3記載の製造法。

【請求項6】 流路断面の大きい流路の断面積が、その前の流路の断面積の2~10倍である請求項4又は5記載の製造法。

【請求項7】 発泡剤含有熱可塑性樹脂の溶融混練物を押出孔の出口から発泡性熱可塑性樹脂粒子のガラス転移温度（以下、Tgと略す）以上の温度の加圧液中に押出し、即時切断して得た粒子を、加圧液中で同温度以上に保持し、次いで冷却する請求項4又は5記載の製造法。

【請求項8】 押出孔の出口から押し出された発泡剤含有熱可塑性樹脂の溶融混練物の切断と、得られた粒子のTg以上の温度の加圧液中の保持を、圧力5kg/cm<sup>2</sup>（ゲージ圧）以上、温度65~95℃の水中で行なう請求項7記載の製造法。

【請求項9】 発泡剤含有熱可塑性樹脂の溶融混練物を押出孔の出口からTg以上の加熱加圧液中に押出し、即時切断して得た粒子を、加圧液中でTg±5℃の温度範囲で徐冷する請求項4又は5記載の製造法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、発泡性熱可塑性樹脂粒子の製造法、詳細には熱可塑性樹脂と発泡剤とを用いた溶融押出法による発泡性熱可塑性樹脂粒子の製造法に関する。

## 【0002】

【従来の技術】 従来、発泡性熱可塑性樹脂粒子、例えば発泡性スチレン系樹脂粒子の製造法としては、スチレン系樹脂の懸濁重合中あるいは重合後に発泡剤を混合し含浸させる懸濁重合法が一般的であるが、この製造法では粒径の均一のものが得られず、ふるい分け等による粒度調整が不可欠であり、また顔料等の着色剤による着色粒

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子の製造も制約が多く、極めて困難である。更に、廃品の発泡性熱可塑性樹脂粒子への再生が不可能である。

【0003】 発泡性熱可塑性樹脂粒子製造の別法として、スチレン系樹脂等の熱可塑性樹脂と発泡剤とを押出機中で溶融混練した後、ペレタイズ用ダイス内に導入し、ダイスの押出孔の出口から加圧水中に押出した後、切断して粒状化する溶融押出造粒法（特開昭48-20423号公報、特開平1-110911号公報等）が知られており、この方法は粒度調整、着色および廃品の再生が容易であるという利点がある。

## 【0004】

【発明が解決しようとする課題】 しかしながら、上記の溶融押出造粒法は、押出機による溶融混練押出で受けた応力が充分に緩和されず、発泡剤含有熱可塑性樹脂の溶融混練物内に残留したまままで造粒されて冷却されるため、発泡に際して粒子の均一な発泡が妨げられ、良好な予備発泡粒子や発泡成形品を安定して得ることができないという課題がある。

## 【0005】

【課題を解決するための手段】 本発明者等は、この様な状況に鑑みて鋭意検討した結果、発泡剤含有熱可塑性樹脂の溶融混練物を、ペレタイズ用ダイス内に導入してダイスの押出孔に向けて流路を流動させ、次いでこの流路よりも流路よりも流路断面積の大きい流路に流入させると、流入時に溶融混練押出で受けた応力が大きく緩和されるため、これを造粒することにより、残留応力が少なく、均一な発泡ができ、良好な予備発泡粒子や発泡成形品が安定して得られる発泡性熱可塑性樹脂粒子を容易に製造できることを見い出し、本発明を完成するに至った。

【0006】 即ち、本発明は、発泡剤含有熱可塑性樹脂の溶融混練物を、ペレタイズ用ダイス内に導入してダイスの押出孔の向けて流路を流動させ、次いでこの流路よりも流路断面積の大きい流路に流入させた後、押出孔を通過させ、その出口から加圧液中に押出し、即時切断して粒子とし、次いで冷却することを特徴とする発泡性熱可塑性樹脂粒子の製造法を提供するものである。

【0007】 本発明で用いる熱可塑性樹脂としては、特に制限はなく、発泡剤により発泡可能な樹脂であればよく、例えばポリスチレン、スチレン-ブタジエン共重合体（耐衝撃性ポリスチレン）、スチレン-（メタ）アクリル酸共重合体、スチレン-無水マレイン酸共重合体、A-S樹脂、A-B-S樹脂等の芳香族ビニル系樹脂、塩化ビニル樹脂、塩化ビニリデン樹脂、塩化ビニル-酢酸ビニル共重合体等の塩化ビニル系樹脂、ポリエチレン、ポリプロピレン等のオレフィン系樹脂、ポリ（メタ）アクリル酸メチル、ポリ（メタ）アクリル酸エチル、メタクリル酸メチル-スチレン共重合体等のアクリル系樹脂、ポリエチレンテレフタート、ポリブチレンテレフタート等のポリエステル系樹脂、ポリカプロラクタム、ヘキ

サメチレンアジポアミド樹脂等のアミド系樹脂、ポリウレタン、ポリカーボネート、ポリエーテルイミド、ポリフェニレンエーテル等の単独あるいは混合物が挙げられ、なかでも芳香族ビニル系樹脂、オレフィン系樹脂が好ましく、特にスチレン系樹脂が好ましい。

【0008】本発明で用いる発泡剤としては、例えば脂肪族炭化水素系発泡剤、ハロゲン化炭化水素系発泡剤等が挙げられ、通常大気圧下での沸点が95℃以下のものを用いる。

【0009】上記脂肪族炭化水素系発泡剤としては、例えばエタン、プロパン、プロピレン、ノルマルブタン、イソブタン、イソブチレン、ノルマルベンタン、イソベンタン、ネオベンタン、シクロベンタン、ヘキサン、石油エーテル等が挙げられ、またハロゲン化炭化水素系発泡剤としては、例えば塩化メチル、塩化エチル、ジクロルエタン、クロロホルム、フルオロメタン、ジフルオロメタン、トリフルオロメタン、ジフルオロエタン、トリフルオロエタン、フルオロクロルメタン、フルオロクロルエタン、ジクロロジフルオロメタン等が挙げられる。なかでも炭素原子数3～6の脂肪族炭化水素、特にノルマルブタン、イソブタン、イソブチレン、ノルマルベンタン、イソベンタンが好ましい。

【0010】発泡剤の使用量は、熱可塑性樹脂100重量部に対して、通常40重量部以下であり、なかでも粒子の凝集がなく、均一なセル径が得られる点で2～10重量部が好ましい。

【0011】本発明の製造法において、発泡剤含有熱可塑性樹脂溶融混練物を得る方法としては、例えば熱可塑性樹脂と発泡剤とを溶融混練機を用いて熱可塑性樹脂の溶融温度以上で溶融混練する方法が挙げられ、通常は単軸押出機、二軸押出機、タンデム型押出機等の押出機を用い、熱可塑性樹脂と発泡剤とを溶融混練した後、これをペレタイズ用ダイス内へ導入する方法を採用する。なかでも発泡剤の分散が良好な点で二軸押出機やタンデム型押出機を用いると好ましい。また、発泡剤は熱可塑性樹脂が半溶融乃至溶融しているところ、例えば押出機の途中の部分から圧入すると好ましい。

【0012】この様に得られた発泡剤含有熱可塑性樹脂溶融混練物は、通常溶融混練機の先に取り付けられたペレタイズ用ダイスの押出孔の出口から、加圧液中に押出した後、即時切断して粒子とする。

【0013】ここで用いるペレタイズ用ダイスとしては、例えば1～数個の導入路と、複数の押出孔と、これらの間にあり、かつその前の流路よりも流路断面積の大きい流路を有するものが挙げられる。

【0014】以下に、図面により本発明で用いるペレタイズ用ダイスの構造を説明する。図1および図2はそぞれ本発明で用いるペレタイズ用ダイスの構造を概略的に示す断面図であり、図3は従来のペレタイズ用ダイスの構造を概略的に示す断面図である。

【0015】図1において、それぞれ1はペレタイズ用ダイス、2は発泡剤含有熱可塑性樹脂溶融混練物の導入のための流路、3は該流路2より流路断面積の大きい流路、4は押出孔、5は押出孔の出口、6は押出孔の出口5を構成する硬化剤層である。また図2において、1、2、4、5および6は図1と同様で、7は導入路2から続く複数の流路、8は該流路7より流路断面積の大きい流路である。さらに図3において、1、2、4、5および6は図1と同様で、7は導入路2から続く複数の流路である。

【0016】本発明で用いるこのようなペレタイズ用ダイスにおいて、流路3又は流路8のような流路断面積の大きい流路の断面積の大きさは、通常流路2又は流路7のようなその前の流路の流路断面積の2倍以上、好ましくは2～10倍であり、また押出孔の大きさは、通常直径0.3～3mm、好ましくは0.5～1mmである。また、押出孔の長さ（流路断面積の大きい流路の終点から押出孔の出口までの距離）は、20mm以下が好ましい。

【0017】切断装置としては、例えば押出孔の出口から押出された発泡剤含有熱可塑性樹脂の溶融混練物を即時高温状態で切断するカッターと加圧液とを内部に有するカッターチャンバーとが取付けられているものが挙げられる。

【0018】加圧液としては、上記粒子の発泡を防止可能な圧力以上に加圧した水、グリコール、エチレングリコール、水とエチレングリコールの混合物等が挙げられ、通常加熱加圧された水を用いる。

【0019】加圧液に加えられる圧力は、通常加圧液の温度における発泡剤の飽和蒸気圧以上の圧力であり、カッターチャンバーに加圧液を満たした場合で通常5kg/cm<sup>2</sup>以上、好ましくは10～20kg/cm<sup>2</sup>である。

【0020】切断装置内の加圧液の温度は、特に限定されず、常温でもよいが、切断して得られた発泡性熱可塑性樹脂粒子のガラス転移温度（以下、Tgと略す）以上、特にTgから加圧下での加圧液の沸点未満の間の温度であると、ペレタイズ用ダイスの流路断面積の大きい流路内では完全に緩和されずに粒子内に応力が残留したとしても、得られた粒子が急冷されないため、残留応力を緩和させる時間を得ることができ、好ましい。水を用いた場合の温度は、通常60～105℃であり、なかでもスチレン系樹脂の場合の温度は、80～95℃が好ましい。

【0021】次いで粒子は、大気圧下でも発泡しなくなる温度まで冷却してもよいが、直ちに冷却せずに加圧液の中でTg以上の温度に、通常2分間以上、好ましくは4～10分間保持（必要に応じてTg以上の温度内で温度を上昇又は低下させてもよい。）あるいはTg前後の温度、好ましくはTg±5度の温度範囲で徐冷して該粒

子内の残留応力の緩和を更に進めた後、冷却、好ましくは平均毎分5°C以上の速度で急冷すると望ましい。冷却された粒子は、次いで常圧下で分離、乾燥される。

【0022】上記造粒後の粒子内の残留応力を緩和する方法は、特に限定されないが、例えばカッターチャンバーから出た発泡剤含有熱可塑性樹脂粒子を、加圧液と共に応力緩和用加圧容器にその上部から供給し、Tg + 5°C以上の温度以上に保持したまま、あるいはTg前後の温度、好ましくはTg ± 5度の温度範囲で徐冷しつつ加圧液中をゆっくり落下させて、粒子内の残留応力を緩和させ、該容器の底部から順次抜き出す方法、カッターチャンバーから出た発泡剤含有熱可塑性樹脂粒子を、加圧液と共に移送管、例えば螺旋状の移送管に流入させ、この管内をTg + 5°C以上の温度以上に保持したまま、あるいはTg前後の温度、好ましくはTg ± 5度の温度範囲で徐冷しつつ加圧液と共に移送させて、粒子内の残留応力を緩和させる方法等が挙げられる。

【0023】また、粒子の冷却方法は、粒子の発泡を防止しつつ冷却できる方法であればよく、例えば加圧下、該粒子と加圧液、又は加圧液を分離した粒子に冷却液を混合して冷却する方法等が挙げられる。

#### 【0024】

【実施例】以下に実施例および比較例を挙げて、本発明を更に詳細に説明するが、本発明はこれにより限定されるものではない。尚、例中の部および%は重量基準である。

#### 【0025】実施例1

本実施例では、図4に示した工程の製造装置を用いて発泡性ポリスチレン粒子を製造した。図4において、11は第1段押出機11aと第2段11bとからなるタンデム型押出機、12は第1段押出機11aのホッパー、13は発泡剤の圧入装置、14はペレタイズ用ダイス、15は熱媒ユニット、16はカッター、17はカッターチャンバー、18は加圧ポンプ、19は熱交換器、20は循環水タンク、21は圧力調整装置、22は応力緩和用加圧容器、23は冷却用加圧容器、24および25はバルブ、26は冷却装置、27は加圧ポンプ、28はバルブ、29は遠心脱水機であり、ペレタイズ用ダイス14は、図1に示す構造を有している。また、太線（加圧ポンプ18および27からバルブ28の間）は加圧された部分を示す。

【0026】ポリスチレン100部とタルク0.02部とからなる混合物を第1段押出機11aと第2段押出機11bとからなるタンデム型押出機11のホッパー12より供給して押出し、次いでブラン7部を第一段押出機11a後半の注入口より供給し、第1段押出機11aおよび第2段押出機11bでポリスチレンとブランとを溶融混練した。この時、樹脂温度は200°C、樹脂圧力は110kg/cm<sup>2</sup>を示した。

【0027】溶融混練した樹脂を、第二段押出機11b 50

の先に取り付けた、図1に示した構造のペレタイズ用ダイス（押出孔の直径：0.7mmφ、押出孔の数：100個、流路3／流路2の断面積比：6.76）を通して、80°C、15kg/cm<sup>2</sup>の加熱加圧水で満たされたカッターチャンバー17の中に80kg/hrの割合で押出し、直ちにカッター16で水中カットして、約0.9mm径の粒子を得た。

【0028】生成した粒子を、6m<sup>3</sup>/hrの加熱加圧水が循環し、80°C、15kg/cm<sup>2</sup>に保持された5100Lの応力緩和用加圧容器22中に移送し、5分間滞留させてさせた。その後、冷却用加圧容器23に移送し、80°Cから25°Cまで5.5分間で急速に冷却した。冷却後、粒子を系外へ取り出した後、遠心脱水機29で脱水し、乾燥して、発泡性ポリスチレン粒子を得た。

【0029】得られた発泡性ポリスチレン粒子は、残留応力が少なく、良好な発泡粒子を容易に製造できるものであった。その性状を表1に示す。尚、発泡性ポリスチレン粒子の性状は以下の方法で測定又は評価した。

- 20 • 発泡性粒子の平均粒子径：100個の発泡性粒子の粒子径をダイヤルゲージで測定し、その平均値を求めた。
- 発泡性粒子の残留応力：発泡性粒子の表面を50倍の超音波顕微鏡写真にとり、その表面の縮模様の程度から目視にて残留応力の多少を判定評価した。
- 発泡性粒子のTg：示差熱分析装置（DSC）にて測定した。

- 発泡倍率（1/嵩密度）：ゲージ圧1kg/cm<sup>2</sup>のスチームで30秒間加熱して発泡させた発泡粒子の嵩密度を求め、その逆数として算出した。
- 30 • 発泡粒子のセル径：上記と同様に発泡させた発泡粒子10個の切断面を50倍の実体顕微鏡写真にとり、そのセルの径を測定し、範囲を求めた。
- 発泡粒子セルの均一性：上記と同様にして50倍の実体顕微鏡写真にとり、セルの均一性を目視にて判定評価した。

#### 【0030】実施例2

溶融混練した樹脂を加熱加圧水の中に押出し、直ちに水中カットして得た生成した粒子を、応力緩和用加圧容器22中に滞留せずに、直接冷却用加圧容器23に移送し、80°Cから25°Cまで7分間かけて冷却した以外は実施例1と同様にして、発泡性ポリスチレン粒子を得た。

【0031】得られた発泡性ポリスチレン粒子は、残留応力が少なく、良好な発泡粒子を容易に製造できるものであった。その性状を表1に示す。

#### 実施例3

溶融混練した樹脂を70°Cの加熱加圧水の中に押出し、直ちに水中カットして得た生成した粒子を、底部から冷却水を導入した応力緩和用加圧容器22中に移送し、70°Cから55°Cまで7.5分間かけて徐冷しつつ粒子の

残留応力を緩和させた後、冷却用加圧容器23に移送し、55℃から25℃まで3分間で急速に冷却した以外は実施例1と同様にして、発泡性ポリスチレン粒子を得た。

【0032】得られた発泡性ポリスチレン粒子は、残留応力が少なく、良好な発泡粒子を容易に製造できるものであった。その性状を表1に示す。

#### 実施例4

図2に示す構造のペレタイズ用ダイス（押出孔の直径：0.8mmφ、押出孔の数：80個、流路8／流路7の断面積比：4）を用いた以外は実施例1と同様にして、発泡性ポリスチレン粒子を得た。

【0033】得られた発泡性ポリスチレン粒子は、残留応力が少なく、良好な発泡粒子を容易に製造できるもの\*

\*であった。その性状を表2に示す。

#### 比較例1

図3に示す構造のペレタイズ用ダイス（押出孔の直径：0.7mmφ、押出孔の数：100個）を用い、溶融混練した樹脂を加熱加圧水の中に押出し、直ちに水中カッタして得た生成した粒子を、応力緩和用加圧容器22中に滞留せずに、直接冷却用加圧容器23に移送し、80℃から25℃まで7分間かけて冷却した以外は実施例1と同様にして、発泡性ポリスチレン粒子を得た。

【0034】得られた発泡性ポリスチレン粒子は、残留応力が多く、良好な発泡粒子が得られないものであった。その性状を表2に示す。

#### 【0035】

#### 【表1】

表1

| 項目                | 実施例1    | 実施例2    | 実施例3    |
|-------------------|---------|---------|---------|
| 発泡性粒子の平均粒子径 (mm)  | 0.9     | 0.9     | 0.9     |
| 発泡性粒子の残留応力        | 少       | 少       | 少       |
| 発泡性粒子のTg (℃)      | 65.0    | 64.5    | 65.0    |
| 発泡倍率(1/嵩密度)(cc/g) | 70      | 68      | 70      |
| 発泡粒子のセル径 (μm)     | 160~180 | 130~200 | 160~200 |
| 発泡粒子セルの均一性        | 均一      | 均一      | 均一      |

#### 【0036】

#### ※※【表2】

表2

| 項目                | 実施例4    | 比較例1   |
|-------------------|---------|--------|
| 発泡性粒子の平均粒子径 (mm)  | 1.0     | 0.9    |
| 発泡性粒子の残留応力        | 少       | 多      |
| 発泡性粒子のTg (℃)      | 65.5    | 65.0   |
| 発泡倍率(1/嵩密度)(cc/g) | 71      | 65     |
| 発泡粒子のセル径 (μm)     | 150~200 | 30~300 |
| 発泡粒子セルの均一性        | 均一      | 不均一    |

#### 【0037】

【発明の効果】本発明の発泡性熱可塑性樹脂粒子の製法によれば、発泡剤含有熱可塑性樹脂の溶融混練物が溶融混練押出で受けた応力を、ペレタイズ用ダイス内で大きく緩和させることができるので、残留応力の少ない良好な発泡粒子を容易に製造できる。

#### 【図面の簡単な説明】

【図1】本発明で用いるペレタイズ用ダイスの構造を概略的に示す断面図である。

【図2】本発明で用いるペレタイズ用ダイスの構造を概略的に示す断面図である。

【図3】従来のペレタイズ用ダイスの構造を概略的に示す断面図である。

【図4】本発明の発泡性熱可塑性樹脂粒子の製法の一例を示す工程図である。

#### 40 【符号の説明】

11 タンデム型押出機

11a 第1段押出機

11b 第2段押出機

12 ホッパー

13 発泡剤の圧入装置

14 ペレタイズ用ダイス

15 熱媒ユニット

16 カッター

17 カッターチャンバー

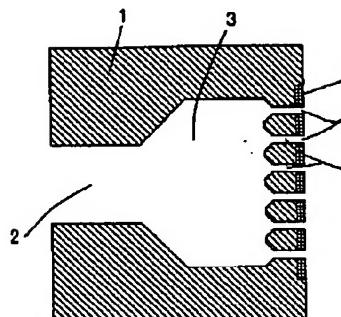
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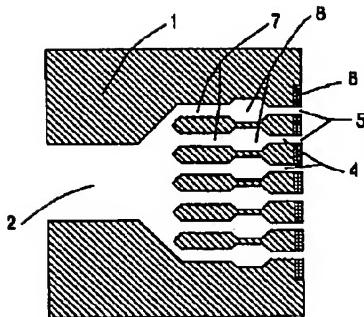
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- |              |                 |
|--------------|-----------------|
| 19 熱交換器      | 24, 24および26 パルプ |
| 20 循環水タンク    | 27 冷却装置         |
| 21 圧力調整装置    | 28 加圧ポンプ        |
| 22 応力緩和用加圧容器 | 29 パルプ          |
| 23 冷却用加圧容器   | 30 遠心脱水機        |

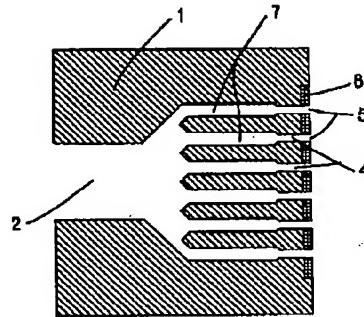
【図1】



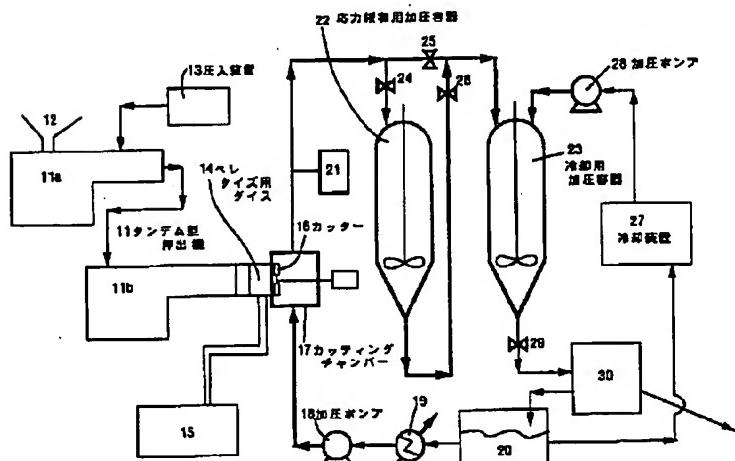
【図2】



【図3】



【図4】



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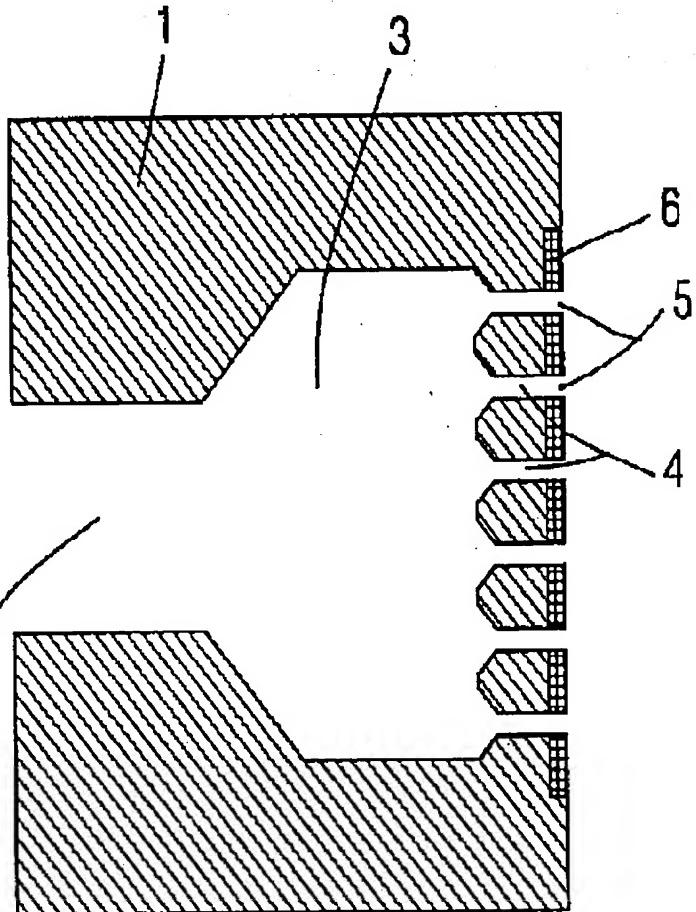
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(54) [Title of Invention]

## A MANUFACTURING METHOD OF FOAMING THERMOPLASTIC RESIN PARTICLES

(57) [Abstract]

[Construction] A thermoplastic resin containing a foaming agent, such as a melt-kneaded mixture of polystyrene and butane, is introduced into pelletizing dies, directing the flow path toward the extrusion holes of the dies, each of which is then guided to a flow path having a larger flow path, such as a flow path having 2~10 times as large a flow cross-sectional area as the flow path, relaxing the stress in the melt-kneaded mixture;



it is then passed through the extrusion holes, extruded into a pressurized fluid from their exits, immediately cut into particles, and cooled.

[Effect] Because the stress received by a melt-kneaded mixture of thermoplastic resin containing a foaming agent in melting, mixing, and extrusion can be relaxed inside pelletizing dies, preferred foam particles with little residual stress can be easily manufactured.

[Claims]

[Claim 1] A manufacturing method of foaming thermoplastic resin particles, wherein thermoplastic resin containing a foaming agent is introduced into pelletizing dies, directing the flow path toward the extrusion holes of the dies, each of which is guided to a flow path having a larger flow path than the flow path; it is then passed through the extrusion holes, extruded into a pressurized fluid from their exits, immediately cut into particles, and cooled.

[Claim 2] The manufacturing method described in Claim 1, wherein a melt-kneaded mixture of thermoplastic resin containing a foaming agent introduced into dies is allowed to flow into multiple flow paths, each of which is subsequently allowed to flow into a flow path having a larger flow path cross section than each flow path, and then passed through extrusion holes.

[Claim 3] The manufacturing method described in Claim 1, wherein a melt-kneaded mixture of thermoplastic resin containing a foaming agent introduced into dies is allowed to flow into a flow path having a larger flow path area than the flow path, and subsequently passed through multiple extrusion holes.

[Claim 4] The manufacturing method described in Claim 1, 2, or 3, wherein the thermoplastic resin is an aromatic vinyl series resin.

[Claim 5] The manufacturing method described in Claim 1, 2, or 3, wherein the thermoplastic resin is a styrene series resin.

[Claim 6] The manufacturing method described in Claim 4 or 5, wherein the cross-sectional area of the flow path having a larger flow path cross section is 2~10 times the cross-sectional area of the previous flow path.

[Claim 7] The manufacturing method described in Claim 4 or 5, wherein a melt-kneaded mixture of thermoplastic resin containing a foaming agent is extruded through exits of extrusion holes into a pressurized liquid at the glass transition temperature (hereinafter abbreviated as Tg) or higher and immediately cut, and the obtained particles are retained at the same temperature or higher in the pressurized liquid and then cooled.

[Claim 8] The manufacturing method described in Claim 7, wherein cutting a melt-kneaded resin containing a foaming agent extruded through exists of extrusion holes and retaining the obtained particles in a pressurized liquid at a temperature Tg or higher are performed in water at a pressure of 5 kg/cm<sup>2</sup> (gauge pressure) or higher and a temperature of 65~95 °C.

[Claim 9] The manufacturing method described in Claim 4 or 5, wherein a melt-kneaded mixture of thermoplastic resin containing a foaming agent is

extruded into a heated and pressurized liquid of Tg in temperature and immediately cut, and the obtained particles are gradually cooled within a temperature range of  $Tg \pm 5$  °C.

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[Detailed description of the invention]

[0001]

[Technical field of the invention]

The present invention relates to a manufacturing method of foaming thermoplastic resin particles, and more particularly, to a manufacturing method of foaming thermoplastic resin particles by the melt extrusion method using a thermoplastic resin and a foaming agent.

[0002]

[Prior Art]

Conventionally, a general manufacturing method of foaming thermoplastic resin particles, such as foaming styrene series resin particles, is the suspension polymerization method, wherein during or after suspension polymerization of a styrene series resin, it is impregnated with a foaming agent. However, by this manufacturing method, uniform particle size cannot be obtained, necessitating grain size adjustment by sieving, etc.. Also there are many restrictions in manufacturing colored particles using a coloring agent such as pigment, making it extremely difficult. Furthermore, recycling of waste materials into foaming thermoplastic resin particles is impossible.

[0003]

Known as another method of manufacturing foaming thermoplastic resin particles is the melt extrusion particle forming method (JP S48-20423, JP H01-110911, etc.), wherein after a thermoplastic resin such as styrene series resin and a foaming agent are melted and kneaded in an extruder, it is introduced into palletizing dies, extruded through exits of extrusion holes of the dies into pressurized water, and cut into particular forms. This method has the advantage that grain size adjustment, coloring, and recycling of waste materials are easy.

[0004]

[Problems to be Solved by Invention]

However, in the melt extrusion particle forming method, because stress received through melt kneading extrusion by the extruder is not sufficiently relaxed but remains in the melt-kneaded mixture of thermoplastic resin containing a foaming agent while particles are formed and cooled, there is the problem that

uniform foaming of the particles is prevented in the foaming process, making it impossible to stably obtain preferable preliminary foam particles or foam molding.

[0005]

[Problem Resolution Means]

As a result of diligent investigation considering such a situation as this, the present inventors completed the present invention by discovering that if a melt-kneaded mixture of thermoplastic resin containing a foaming agent is introduced into pelletizing dies, its flow path is directed toward the extrusion holes of the dies, and it is allowed to flow into a flow path having a larger flow path cross-sectional area, because the stress received in extruding the melt-kneaded mixture is greatly relaxed, by forming it into particles, it is possible to manufacture easily foaming thermoplastic resin particles, which allow obtaining preferable preliminary foam particles and foam molds having little remaining stress and uniform foaming.

[0006]

Namely, the present invention provides a manufacturing method of foaming thermoplastic resin particles, wherein a melt-kneaded mixture of thermoplastic resin containing a foaming agent is introduced into pelletizing dies, its flow path is directed toward the extrusion holes of the dies, and it is guided to a flow path having a larger flow path cross-sectional area, passed through the extrusion holes, extruded into a pressurized fluid from their exits, immediately cut into particles, and then cooled.

[0007]

The thermoplastic resin used in the present invention is not particularly restricted but may be any resin which can be foamed by a foaming agent, etc. Listed as the examples are aromatic vinyl series resins such as polystyrene, styrene-butadiene copolymer (shock-resistant polystyrene), styrene - (meth)acrylic acid copolymer, styrene - maleic anhydride copolymer, AS resin, and ABS resin; polyvinyl chloride series resins such as polyvinyl chloride resin, polyvinylidene chloride resin, and polyvinyl chloride - polyvinyl acetate copolymer; olefin series resins such as polyethylene and polypropylene; acrylic series resins such as methyl poly(meth)acrylate, ethyl poly(meth)acrylate, and methyl methacrylate - styrene copolymer; polyester series resins such as polyethylene terephthalate and polybutylene terephthalate; amide series resins such as polycaprolactam and hexamethylene adipamide resin; and single or mixture of polyurethane,

polycarbonate, polyether-imide, and polyphenylene ether, among which styrene series resins are preferred.

[0008]

Listed for example as the foaming agent used in the present invention are aromatic hydrocarbon series foaming agents, halogenated hydrocarbon series foaming agents, etc., among which those having a boiling point of 95 °C or lower under the normal atmospheric pressure are used.

[0009]

Listed for example as said aromatic hydrocarbon series foaming agents are ethane, propane, propylene, normal butane, isobutane, isobutylene, normal pentane, isopentane, neopentane, cyclopentane, hexane, and petroleum ether, and also listed for example as said halogenated hydrocarbon series foaming agents are methyl chloride, ethyl chloride, dichloroethane, chloroform, fluoromethane, difluoromethane, trifluoromethane, difluoro ethane, trifluoroethane, fluorochloromethane, fluorochloroethane, and dichlorodifluoromethane. Among them, aliphatic hydrocarbons of 3~6 in the number of carbon atoms, especially normal butane, isobutane, isobutylene, normal pentane, and isopentane are preferred.

[0010]

The amount of foaming agent used is usually 40 weight parts or less per 100 weight parts of the thermoplastic resin, among which 2~10 weight parts is preferred in the respect that there is no coagulation of particles and that a uniform cell size is obtained.

[0011]

In the manufacturing method of the present invention, listed for example as the method of obtaining a melt-kneaded mixture of thermoplastic resin containing a foaming agent is the method wherein a thermoplastic resin and a foaming agent are melted and kneaded at the melting temperature of the thermoplastic resin or higher using a melt kneading machine. Usually adopted is a method wherein an extruder such as a single-spindle extruder, a double-spindle extruder, and a tandem-type extruder to melt-knead a thermoplastic resin and a foaming agent and then introduce it into palletizing dies. Particularly preferred is the use of a double-spindle extruder or a tandem-type extruder for good dispersion of the foaming agent. Also, it is preferred to inject the foaming agent where the thermoplastic resin is half melted or melted, for example the middle part of the extruder.

[0012]

The melt-kneaded mixture of thermoplastic resin containing a foaming agent obtained in this way is extruded from the exits of the extrusion holes of the palletizing dies into a pressurized liquid and cut into particles.

[0013]

Listed for example as the palletizing dies used here are those having one to several introduction paths, multiple extrusion holes, and flow paths which are between them and have larger flow path cross-sectional areas than the previous flow paths.

[0014]

The structure of palletizing dies used in the present invention is explained below with reference to the drawings. Fig. 1 and Fig. 2 are cross-sectional views showing overview structures of the palletizing dies used in the present invention, and Fig. 3 is a cross-sectional view showing an overview structure of a conventional palletizing dies.

[0015]

In Fig. 1, 1 represents palletizing dies, 2 is a flow path for introducing a melt-kneaded mixture of thermoplastic resin containing a foaming agent, 3 is a flow path having a larger cross-sectional area than the flow path 2, 4 are extrusion holes, 5 are their exits, and 6 are hardening agent layers constituting the exits 5. Also in Fig. 2, indicated as 1, 2, 4, 5, and 6 are the same as in Fig. 1, 7 are multiple flow paths continuing from the introduction flow path 2, and 8 are flow paths having larger flow-path cross-sectional areas than the flow paths 7. Furthermore in Fig. 3, indicated as 1, 2, 4, 5, and 6 are the same as in Fig. 1, and 7 are multiple flow paths continuing from the introduction flow path 2.

[0016]

In such palletizing dies used in the present invention, the cross-sectional area of the flow path such as the flow path 3 and the flow path 8 having a larger flow-path cross-sectional area is usually twice or more, preferably 2~10 times as large as the flow-path cross-sectional area of the preceding flow path such as the flow path 2 and the flow path 7, and the size of the extrusion holes is usually 0.3~3 mm, preferably 0.5~1 mm in diameter. Also, the length (distance from the end point of the flow path having a larger flow-path cross-sectional area to the exits of the extrusion holes) of the extrusion holes is preferably 20 mm or smaller.

[0017]

Listed for example as the cutting device is one equipped with a cutter which cuts the melt-kneaded mixture of thermoplastic resin containing a foaming agent extruded from the exits of the extrusion holes immediately under a high-temperature state, and a cutter chamber containing internal pressurized liquid.

[0018]

Listed as the pressurized liquid are water, glycol, ethylene glycol, a mixture of water and ethylene glycol, etc. which are pressurized above the pressure at which foaming of said particles can be prevented. Heated and pressurized water is usually used.

[0019]

The pressure applied to the pressurized liquid is usually a pressure above the saturated vapor pressure of the foaming agent at the temperature of the pressurized liquid, which is usually 5 kg/cm<sup>2</sup> and preferably 10~20 kg/cm<sup>2</sup> when the pressurized liquid is filled in the cutter chamber.

[0020]

The temperature of the pressurized liquid inside the cutting device is not particularly restricted but can be room temperature. However, if it is a temperature above the glass transition temperature (hereinafter abbreviated as Tg) of the foaming thermoplastic resin particles obtained by cutting, especially if it is a temperature between Tg and below the boiling point of the pressurized liquid under pressure, inside the flow path of the palletizing dies having a large flow-path cross-sectional area, even if stress remains inside the particles without completely relaxing, because the obtained particles are not rapidly cooled, time for relaxing residual stress can be obtained, making it preferable. The temperature when water is used is usually 60~105 °C, and especially 80~95 °C is preferred as the temperature when styrene series resins are used.

[0021]

Next, although the particles may be cooled to a temperature where no foaming occurs even under the atmospheric pressure, it is desirable that it not be cooled immediately but held in the pressurized liquid at a temperature above the temperature Tg usually for over 2 minutes, and preferable for 4~10 minutes (the temperature may be increased or decreased within the temperature range above Tg), or be gradually cooled at a temperature around Tg, preferably within the temperature range of Tg ± 5 °C to promote relaxation of residual stress in the

particles, and then cooled, preferably rapidly cooled at an average rate of 5 °C per minute. The cooled particles are next separated and dried under normal pressure.

[0022]

The method for relaxing said residual stress inside the particles after particle formation is not particularly specified; but listed for example are a method wherein particles of the thermoplastic resin containing a foaming agent which came out of the cutter are fed to a pressurizing container for stress relaxation from its top, and while being retained at a temperature above  $T_g + 5$  °C or gradually cooled around the temperature  $T_g$  or preferably within a temperature range of  $T_g \pm 5$  °C, the pressurized liquid is slowly lowered to relax residual stress inside the particles and chronologically taken out from the bottom of said container; a method wherein particles of the thermoplastic resin containing a foaming agent which came out of the cutter chamber are allowed to flow into a transfer pipe, for example a spiral transfer pipe, together with the pressurized liquid, and while retaining the interior of the pipe at a temperature above  $T_g + 5$  °C or gradually cooling it to a temperature around  $T_g$ , preferably within a temperature range of  $T_g \pm 5$  °C, it is transferred together with the pressurized liquid to relax residual stress inside the particles.

[0023]

Also, the method of cooling the particles may be any method which can cool the particles while preventing them from foaming. Listed for example is a method wherein a cooling liquid is mixed with the particles and pressurized liquid or the particles with the pressurized liquid separated under pressure to perform the cooling.

[0024]

#### [Examples (Embodiments)]

The present invention is explained in detail hereafter, listing embodiments and a comparative example. However, the present invention is not limited by these. Note that part and % is the examples are in weight.

[0025]

**Embodiment 1:** In this embodiment, foaming polystyrene particles were manufactured using a manufacturing apparatus having the manufacturing processes shown in Fig. 4. In Fig. 4, indicated as 11 is a tandem-type extruder composed of a first-stage extruder 11a and a second-stage 11b, 12 is a hopper of the first-stage extruder 11a, 13 is a foaming agent injector, 14 is palletizing dies, 15 is a heat transfer unit, 16 is a cutter, 17 is a cutter chamber, 18 is a pressurizing pump, 19 is a heat exchanger, 20 is a circulating water tank, 21 is a pressure adjustment

device, 22 is a pressurizing container for stress relaxation, 23 is a pressurizing container for cooling, 24 and 25 are valves, 26 is a cooling device, 27 is a pressurizing pump, 28 is a valve, and 29 is a centrifugal dehydrator, wherein the palletizing dies 14 has a structure shown in Fig. 1. Also, a bold line (between the pressurizing pumps 18 and 27 and the valve 28) indicates a pressurized portion.

[0026] A mixture composed of 100 parts of polystyrene and 0.02 parts of talc is fed and extruded from the hopper 12 of the tandem-type extruder 11 composed of the first-stage extruder 11a and the second-stage extruder 11b, next 7 parts of butane is fed from an inlet of the rear half of the first-stage extruder 11a, and polystyrene and butane are melt-kneaded with the first-stage extruder 11a and the second-stage extruder 11b. At this time, the resin temperature indicated 200 °C, the resin pressure indicated 110 kg/cm<sup>2</sup>.

[0027]

A melt-kneaded resin is extruded through palletizing dies (the diameter of extrusion holes: 0.7 mmφ, the number of extrusion holes: 100, cross-sectional area ratio of the flow path 3 / the flow path 2: 6.76) having a structure shown in Fig. 1 attached to the tip of the second-stage extruder 11b into the cutter chamber 17 filled with heated and pressurized water of 80 °C and 15 kg/cm<sup>2</sup> at a rate of 80 kg/hr, and immediately cut in water by the cutter 16, obtaining particles of about 0.9 mm in diameter.

[0028]

The formed particles were transferred into the pressurizing container for stress relaxation 22 of 500 L wherein heated and pressurized water of 6 m<sup>3</sup>/hr is circulated and kept at 80 °C and 15 kg/cm<sup>2</sup>, and were left there for 5 minutes. Afterwards, they were transferred to the pressurizing container for cooling 23 and cooled rapidly from 80 °C to 25 °C over 5.5 minutes. After cooling, the particles were taken out of the system, dehydrated with the centrifugal dehydrator 29, and dried, obtaining foaming polystyrene particles.

[0029]

The obtained foaming polystyrene particles had little residual stress, from which good foam particles could be easily manufactured. The properties are listed in Table 1. Note that the properties of the foaming polystyrene particles were measured or evaluated by the following methods. • Average particle size of the foam particles: Particle sizes of 100 foam particles were measured using a dial gauge, and their average value was computed. • Residual stress of the foam particles: Ultrasound microscopic photographs of the foam particle surfaces were

taken at a magnification of 50 times, and the degrees of residual stress were estimated visually from the degrees of stripe patterns on their surfaces. • Tg of the foam particles: Measured using a differential scanning calorimeter (DSC). • Expansion ratio (1 / bulk density): Bulk density of foam particles which were foamed by heating 30 seconds with steam of 1 kg/cm<sup>2</sup> in gauge pressure was obtained, and its inverse was computed. Cell diameters of the foam particles: Stereoscopic microscope photos of 50-time magnification of cut cross sections of ten foam particles foamed in the same manner as in the above were taken, and their cell diameters were measured to obtain the range. • Uniformity of the foam particles: Stereoscopic microscope photos of 50-time magnification were taken in the same was as in the above, and uniformity of the cells was visually estimated.

[0030]

**Embodiment 2:**

A melt-kneaded resin was extruded into heated and pressurized water and immediately cut to form particles. Foaming polystyrene particles were obtained in the same manner as in Embodiment 1 except that the obtained particles were not left in a pressurizing container for stress relaxation 22 but directly transferred to a pressurizing container for cooling 23, and cooled from 80 °C to 25 °C over 7 minutes.

[0031]

The obtained foaming polystyrene particles had little residual stress, from which good foam particles could be easily manufactured. The properties are listed in Table 1. Embodiment 3: A melt-kneaded resin was extruded into heated and pressurized water of 70 °C, immediately cut in water to form particles. Foaming polystyrene particles were obtained in the same manner as in Embodiment 1 except that the obtained particles were transferred into a pressurizing container for stress relaxation 22 wherein cooling water is introduced from the bottom portion, gradually cooled from 70 °C to 55 °C over 7.5 minutes to relax residual stress of the particles, transferred into a pressurizing container for cooling 23, and rapidly cooled from 55 °C to 25 °C over 3 minutes.

[0032]

The obtained foaming polystyrene particles had little residual stress, from which good foaming particles could be easily manufactured. The properties are listed in Table 1. Embodiment 4: Foaming polystyrene particles were obtained in the same manner as in Embodiment 1 except that palletizing dies (the diameter of extrusion holes: 0.8 mmΦ, the number of extrusion holes: 80, cross-sectional area ratio of the flow path 8 / the flow path 7: 4) of a structure shown in Fig. 2 was used.

[0033]

The obtained foaming polystyrene particles had little residual stress, from which good foaming particles could be easily manufactured. The properties are listed in Table 2. Comparative Example 1: Foaming polystyrene particles were obtained in the same manner as in Embodiment 1 except that particles formed by extruding a melt-kneaded resin was extruded into heated and pressurized water using palletizing dies (the diameter of extrusion holes: 0.7 mmφ, the number of extrusion holes: 100) of a structure shown in Fig. 3 and cutting immediately in water were not left in the pressurizing container for stress relaxation 22 but directly transferred to the pressurizing container for cooling 23 and cooled from 80 °C to 25 °C over 7 minutes.

[0034]

The obtained foaming polystyrene particles had much residual stress, from which good foam particles could not be obtained. The properties are listed in Table 2.

[0035]

[Table 1]

Table 1

| Item  | Embodiment 1 | Embodiment 2 | Embodiment 3 |
|---|--------------|--------------|--------------|
| Average particle size (mm) of foaming particles | 0.9          | 0.9          | 0.9          |
| Residual stress of foaming particles            | Little       | Little       | Little       |
| Tg (°C) of foaming particles                    | 65.0         | 64.5         | 65.0         |
| Expansion rate (1 / bulk density) (cc/g)        | 70           | 68           | 70           |
| Cell diameter of foam particles (μm)            | 160~180      | 130~200      | 160~200      |
| Uniformity of foam particle cells               | Uniform      | Uniform      | Uniform      |

[0036]

[Table 2]

Table 2

| Item  | Embodiment 4 | Comparative Example<br>1 |
|---|--------------|--------------------------|
| Average particle size<br>(mm) of foaming<br>particles | 1.0          | 0.9                      |
| Residual stress of<br>foaming particles               | Little       | Little                   |
| Tg (°C) of foaming<br>particles                       | 65.5         | 65.0                     |
| Expansion rate (1 / bulk<br>density) (cc/g)           | 71           | 65                       |
| Cell diameter of foam<br>particles ( $\mu\text{m}$ )  | 150~200      | 30~300                   |
| Uniformity of foam<br>particle cells                  | Uniform      | Nonuniform               |

[0037]

## [Effect of the Invention]

According to the manufacturing method of foaming thermoplastic resin particles of the present invention, because stress received by a melt-kneaded mixture of thermoplastic resin containing a foaming agent through melt kneading extrusion can be greatly relaxed in palletizing dies, good foam particles having little residual stress can be easily manufactured.

[Brief Explanations of Drawings]

[Figure 1] A cross-sectional view showing an outline structure of the palletizing dies used in the present invention.

[Figure 2] A cross-sectional view showing an outline structure of the palletizing dies used in the present invention.

[Figure 3] A cross-sectional view showing an outline structure of a conventional palletizing dies.

[Figure 4] A manufacturing process diagram showing an example of the manufacturing method of foaming thermoplastic resin particles of the present invention.

[Explanations of Codes]

- 11: Tandem-type extruder
  - 11a: First-stage extruder
  - 11b: Second-stage extruder
  - 12: Hopper
  - 13: Foaming agent injector
  - 14: Pelletizing dies
  - 15: Heat transfer unit
  - 16: Cutter
  - 17: Cutter chamber
  - 18: Pressurizing pump
  - 19: Heat exchanger
  - 20: Circulating water tank
  - 21: Pressure adjustment device
  - 22: Pressurizing container for stress relaxation
  - 23: Pressurizing container for cooling
  - 24, 24, 26: valves
  - 27: Cooling device
  - 28: Pressurizing pump
  - 29: Valve
  - 30: Centrifugal dehydrator
-

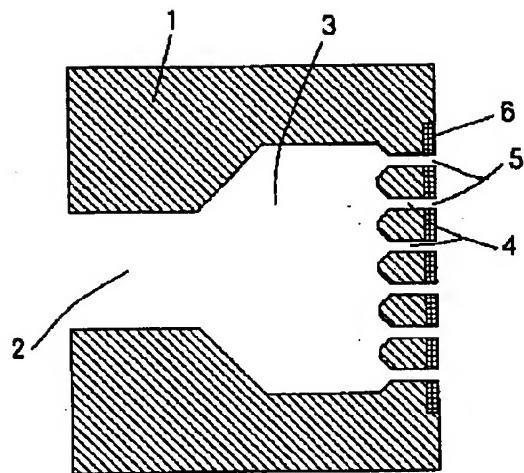


Fig. 1. A cross-sectional view showing an outline structure of the palletizing dies used in the present invention.

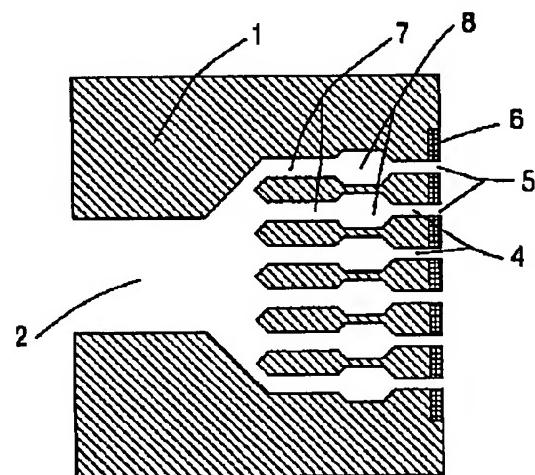


Fig. 2. A cross-sectional view showing an outline structure of the palletizing dies used in the present invention.

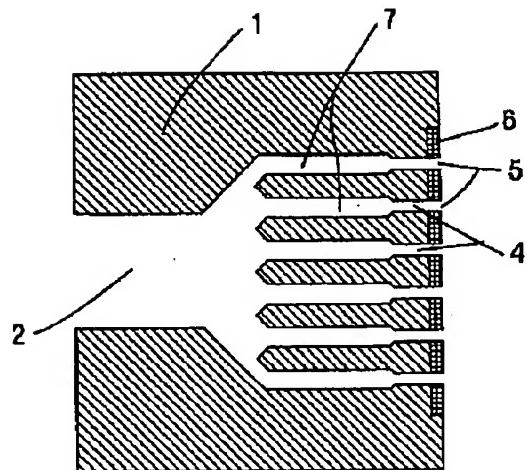


Fig. 3. A cross-sectional view showing an outline structure of a conventional palletizing dies.

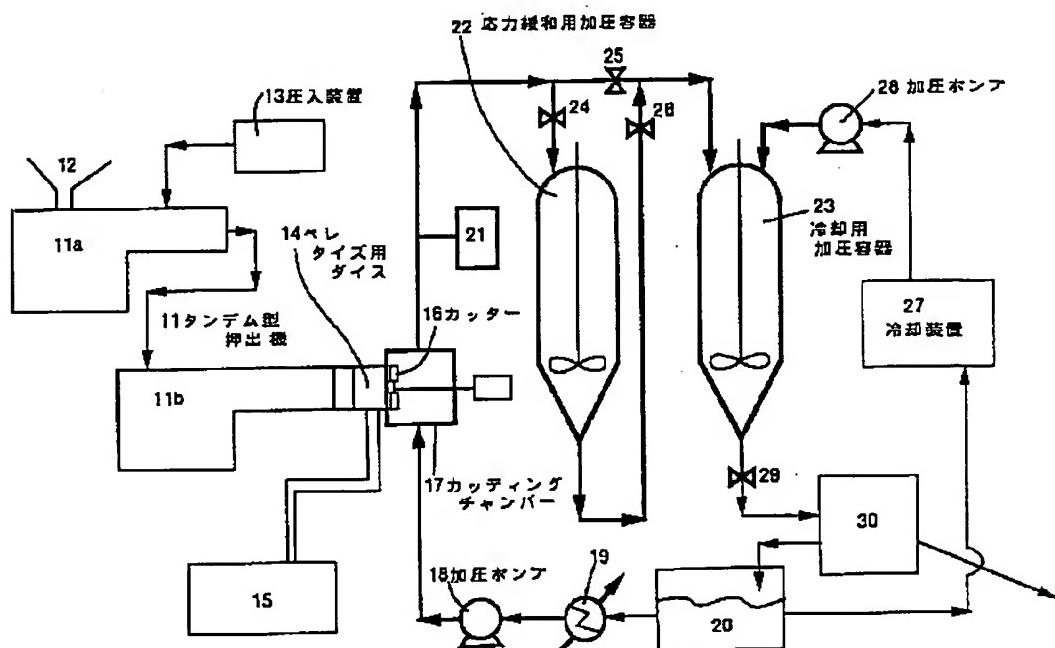


Fig. 4. A manufacturing process diagram showing an example of the manufacturing method of foaming thermoplastic resin particles of the present invention.

11: Tandem-type extruder, 13: Injector, 14: Pelletizing dies, 16: Cutter, 17: Cutting chamber, 18: Pressurizing pump, 22: Pressuring container for stress relaxation, 23: Pressurizing container for cooling, 27: Cooling device, 28: Pressurizing pump.